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Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):

Wu, Q., Christensen, J. M., Temel, B., Grunwaldt, J-D., & Jensen, A. D. (2011). *Supported Cu/Group VIII metal alloys for synthesis of alcoholic fuels from syngas*. Abstract from The 22nd North American Catalysis Society Meeting, Detroit, United States.

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Supported Cu/Group VIII metal alloys for synthesis of alcoholic fuels from syngas

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Introduction

Alternatives to petroleum-derived fuels and chemicals are being sought in an effort to enhance energy security and the air quality through development of novel technologies for the production of synthetic fuels and chemicals using renewable energy sources such as biomass [1,2]. Higher alcohols (C₂₊ alcohols) are being considered as potential alternative synthetic fuels, as they can be produced by syngas derived from biomass [2,3]. There are two processes involved in this technique: First, syngas (CO and H₂) is thermo-chemically formed by the gasification of biomass, and then the syngas is converted into higher alcohols [3].

Catalyst systems of copper combined with group VIII metals such as Co [4] and Ni [5] have shown interesting results for higher alcohols synthesis (HAS) with respect to selectivity and activity. Recently it was reported that nano-particles outside/inside carbon nanotubes (CNTs) showed better performances than nano-particles on conventional supports [6]. It might thus be envisioned that Cu-Ni/Co supported on CNTs could have a better performance for HAS as well. This work provided a systematic study of Cu-Ni or Cu-Co catalysts for HAS from syngas. Different Cu/Ni (or Co) ratios, supports and operating conditions were employed. The work included activity evaluations and spectroscopic investigations.

Materials and Methods

Cu/Group VIII metal based catalysts were prepared by impregnation (with ultrasonic treatment). Nitrate salts of Cu, Co, and Ni as well as CNTs (Sigma-Aldrich) and Al₂O₃ were used for preparation of catalysts. All catalyst precursors were dried at 120 °C overnight and calcined in air or N₂ (CNT based cats.) at 400 °C for 4 h. Performance of catalysts for HAS from syngas has been evaluated in a fixed-bed continuous-flow reactor with a GC-FID/TCD detection system. Prior to the reaction, samples of the oxide precursor of catalysts were pre-reduced in situ by a 10% H₂ in N₂ gaseous mixture for 12 h at 300 °C with a heating rate of 1 °C/min. Typical operating conditions are: P = 60-100 bar; T = 250-325 °C; GHSV = 2000 h⁻¹; Feed: H₂/CO=1 (v/v). TPR was carried out for identifying the reduction temperatures of catalysts and complementary in-situ XAS experiments are conducted. Particle sizes and phase composition were investigated using in-situ XRD. The specific surface areas of both fresh and used catalysts were determined by N₂ adsorption at 77 K. In-situ TEM was used to study the catalyst morphology in H₂ gas flow from 25 to 600 °C.

Results and Discussion

The CO conversion and productivity of alcohols are enhanced by increasing pressure and temperature. However, the selectivity to alcohols is decreased by increasing temperature, while the selectivity to hydrocarbons is increased. The TPR revealed that a strong interaction occurs between copper and nickel in the mixed oxide catalysts since they were more easily reduced than the pure CuO and NiO oxides.

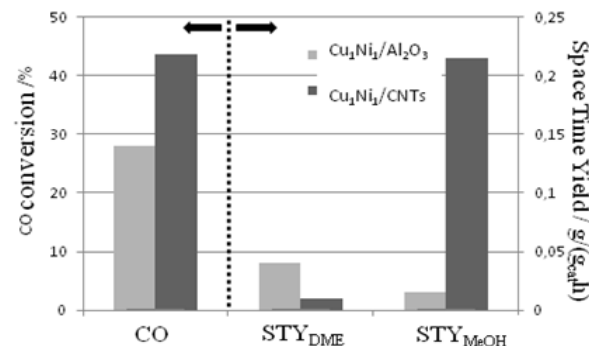


Figure 1. CO conversion, space time yield (STY, g/(g_{cat}h)) of methanol (MeOH) and dimethyl ether (DME) at 100 bar, 300 °C, GHSV 2000 h⁻¹ and V(H₂)/V(CO)=1 over Cu₂Ni₁/CNTs and Cu₂Ni₁/Al₂O₃ catalysts (20 wt% Cu and Ni for both catalysts). Time on stream +50 h.

Figure 1 shows that Cu-Ni catalysts supported on Al₂O₃ and CNTs exhibited different catalytic behaviors for CO hydrogenation. The CNTs supported catalyst showed much higher activity than the Al₂O₃ supported one. The former one mainly produced methanol, while the latter one produced DME. This is due to the Lewis acidic sites of γ -Al₂O₃ that can dehydrate methanol to DME. The current work is focused on changing the catalytic selectivity of the catalysts towards higher alcohols by modifying the basicity of the catalysts with alkali and other promoters.

Significance

This work is significant for an industrial utilization for alcoholic fuels production. The nature of catalysts and reaction mechanism may be inferred from the presented results.

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